

a!

- b) pressurizing said fluid so as to cause the subterranean formation to fracture and allow the proppant materials to enter said crack;
- c) acidifying said fluid so as to change the oil-wet proppant materials into water-wet proppant materials and;
- d) washing said well with an aqueous based wash solution.

29. (NEW) The method of claim 28 wherein said fluid is acidified by carbon dioxide from the formation.

30. (NEW) The method of claim 28 wherein said fluid is acidified by hydrogen sulfide from the formation.

REMARKS REGARDING AMENDMENTS:

Applicant respectfully submits that no new matter is introduced by the proposed amendments to the claims.

Support for the above amendments to the claims can be found in the original specification as filed in the following locations:

Amendment to Claim:	Disclosure in Specification Supporting Amendment:
22	Page 14, line 19 - Page 15, line 15
25	Page 16, line 12 - Page 17, line 8
28	Page 17, line 9 - Page 18, line 6
23, 24, 26, 27, 29, 30	Page 9, lines 26-30

One of skill in the art should realize that carbon dioxide and hydrogen sulfide may come from the formation. Additionally, in the book COMPOSITION AND PROPERTIES OF DRILLING AND COMPLETION FLUIDS, 5th Edition, incorporated by reference on page 6, lines 10-13 of the specification, the authors teach that carbon dioxide and hydrogen sulfide from the formation may acidify drilling fluids. (See pages 474-480, a copy of which is included with this paper).

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Serial No.: 09/887,138
Applicant: PATEL
11836.0582.CPUS02

the specification, the authors teach that carbon dioxide and hydrogen sulfide from the formation may acidify drilling fluids. (See pages 474-480, a copy of which is included with this paper).

The claims and amended claims are submitted as being clearly distinct and patentable over the art of record and therefore Applicant respectfully requests their entry and allowance by the Examiner.

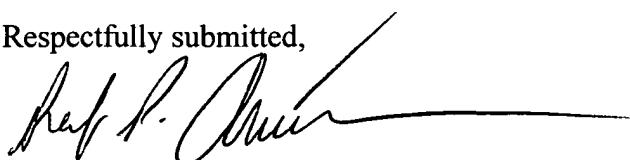
The Commissioner is authorized to charge \$360.00 for the new claims (3 independent + 6 dependent) as indicated on the enclosed FORM 2038.

Applicant hereby requests for any extension of time that may be deemed necessary to further the prosecution of this application. Applicant's representative hereby authorizes the Commissioner to charge any additional fees which may be required, or credit any overpayment, to the Deposit Account No. 01-2508, referencing Order No. 11836.0582.CPUS02.

In order to facilitate the resolution of any issues or questions presented by this paper, Applicant respectfully requests that the Examiner directly contact the undersigned by phone to further the discussion.

In order to promote the prosecution of this application, the Examiner is hereby authorized to contact the undersigned by electronic mail. Please address all e-mail to:
auerbachr@howrey.com.

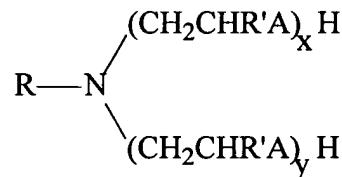
Respectfully submitted,



Robert P. Auerbach
Patent Agent
Reg. No. 46,525
Date: 11 MAR 2002

CLAIMS SHOWING AMENDMENTS OF Preliminary Amendment
WHAT IS CLAIMED IS:

1. A method of electrically logging a subterranean well, the method comprising:
 - a) drilling the subterranean well with an invert emulsion drilling fluid, wherein said fluid includes: an oleaginous fluid; a non-oleaginous fluid; and an amine surfactant having the structure



wherein R is a C₁₂-C₂₂ aliphatic hydrocarbon; R' is an independently selectable from hydrogen or C₁ to C₃ alkyl; A is NH or O, and 1 ≤ x+y ≤ 3;

- b) adding acid to the invert emulsion drilling fluid in a sufficient amount to reverse the filtercake solids from being oil-wet to being water-wet; and
- c) electrically logging said well.

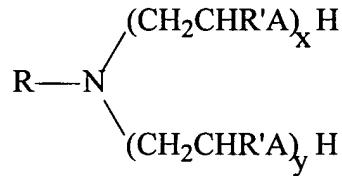
2. The method of claim 1 wherein said oleaginous fluid comprising from 5 to about 100% by volume of the oleaginous fluid of a material selected from a group consisting of esters, ethers, acetals, di-alkylcarbonates, hydrocarbons, and combinations thereof.
3. The method of claim 1 wherein said non-oleaginous liquid is an aqueous liquid.
4. The method of claim 3 wherein said aqueous liquid is selected from the group consisting of sea water, a brine containing organic or inorganic dissolved salts, a liquid containing water-miscible organic compounds, and combinations thereof.

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5. The method of claim 1 wherein said amine surfactant is selected from diethoxylated tallow amine; diethoxylated soya amine; N-aliphatic-1,3-diaminopropane wherein the aliphatic group is a C₁₂ to C₂₂ hydrocarbon; or combinations thereof.

6. A method of gravel packing a downhole area of a subterreanean well, said method comprising:

a) forming a mixture of a gravel packing material and an invert emulsion drilling fluid, wherein said fluid includes: an oleaginous fluid; a non-oleaginous fluid; an amine surfactant having the structure



wherein R is a C₁₂-C₂₂ aliphatic hydrocarbon; R' is an independently selectable from hydrogen or C₁ to C₃ alkyl; A is NH or O, and 1 ≤ x+y ≤ 3;

- b) injecting said mixture of gravel packing material and invert emulsion into a subterranean well so as to gravel pack the downhole area ; and
- c) adding acid to said fluid so as to change the oil-wet gravel packing materials into water-wet gravel packing materials and;
- d) washing said well with an aqueous based wash solution.

7. The method of claim 6 wherein said oleaginous fluid comprising from 5 to about 100% by volume of the oleaginous fluid of a material selected from a group consisting of esters, ethers, acetals, di-alkylcarbonates, hydrocarbons, and combinations thereof.

8. The method of claim 6 wherein said non-oleaginous liquid is an aqueous liquid.

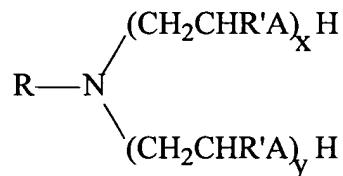
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9. The method of claim 8 wherein said aqueous liquid is selected from the group consisting of sea water, a brine containing organic or inorganic dissolved salts, a liquid containing water-miscible organic compounds, and combinations thereof.

10. The method of claim 6 wherein said amine surfactant is selected from diethoxylated tallow amine; diethoxylated soya amine; N-aliphatic-1,3-diaminopropane wherein the aliphatic group is a C₁₂ to C₂₂ hydrocarbon; or combinations thereof.

11. A method of injecting drill cuttings into a downhole area of a subterreanean well, said method comprising:

a) collecting the drilling cuttings from a subterreanean well drilled with an invert emulsion drilling fluid, said invert emulsion drilling fluid includes: an oleaginous fluid; a non-oleaginous fluid; an amine surfactant having the structure



wherein R is a C₁₂-C₂₂ aliphatic hydrocarbon; R' is an independently selectable from hydrogen or C₁ to C₃ alkyl; A is NH or O, and 1 ≤ x+y ≤ 3;

- c) adding acid to said drilling cuttings so as to change the drilling cuttings from being oil wet to being water wet;
- d) grinding and suspending said cuttings in an aqueous based injection fluid; and
- e) injecting said suspension of cuttings in injecting fluid into a disposal zone in a subterranean well.

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12. The method of claim 11 wherein said oleaginous fluid comprising from 5 to about 100% by volume of the oleaginous fluid of a material selected from a group consisting of esters, ethers, acetals, di-alkylcarbonates, hydrocarbons, and combinations thereof.

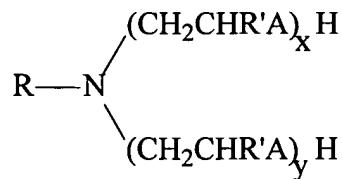
13. The method of claim 11 wherein said non-oleaginous liquid is an aqueous liquid.

14. The method of claim 13 wherein said aqueous liquid is selected from the group consisting of sea water, a brine containing organic or inorganic dissolved salts, a liquid containing water-miscible organic compounds, and combinations thereof.

15. The method of claim 11 wherein said amine surfactant is selected from diethoxylated tallow amine; diethoxylated soya amine; N-aliphatic-1,3-diaminopropane wherein the aliphatic group is a C₁₂ to C₂₂ hydrocarbon; or combinations thereof.

16. A method of fracturing a subterranean formation, the subterranean formation being in fluid communication with the surface via a well, the method comprising:

- a) injecting a fracturing fluid into said well, wherein said fracturing fluid includes: an oleaginous fluid; and an amine surfactant having the structure



wherein R is a C₁₂-C₂₂ aliphatic hydrocarbon; R' is an independently selectable from hydrogen or C₁ to C₃ alkyl; A is NH or O, and 1 ≤ x+y ≤ 3; and oil-wet propant material;

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- b) pressurizing said fluid so as to cause the subterranean formation to fracture and allow the proppant materials to enter said crack;
- c) adding acid to said fluid so as to change the oil-wet proppant materials into water-wet proppant materials and;
- d) washing said well with an aqueous based wash solution.

17. The method of claim 16 wherein said oleaginous fluid comprising from 5 to about 100% by volume of the oleaginous fluid of a material selected from a group consisting of esters, ethers, acetals, di-alkylcarbonates, hydrocarbons, and combinations thereof.

18. The method of claim 16 wherein the fracturing fluid further includes a non-oleaginous liquid.

19. The method of claim 18 wherein said non-oleaginous liquid is selected from the group consisting of sea water, a brine containing organic or inorganic dissolved salts, a liquid containing water-miscible organic compounds, and combinations thereof.

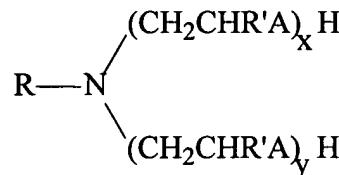
20. The method of claim 16 wherein said amine surfactant is selected from diethoxylated tallow amine; diethoxylated soya amine; N-aliphatic-1,3-diaminopropane wherein the aliphatic group is a C₁₂ to C₂₂ hydrocarbon; or combinations thereof.

21. The method of claim 16 wherein the proppant material is selected from the group consisting of quartz gravel, sand, glass beads, ceramic pellets, and combinations thereof.

22. (NEW) A method of electrically logging a subterranean well, the method comprising:

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a) drilling the subterranean well with an invert emulsion drilling fluid,
wherein said fluid includes: an oleaginous fluid; a non-oleaginous fluid; and an amine
surfactant having the structure



wherein R is a C₁₂-C₂₂ aliphatic hydrocarbon; R' is an independently
selectable from hydrogen or C₁ to C₃ alkyl; A is NH or O, and 1 ≤ x+y ≤ 3;

b) acidifying the invert emulsion drilling fluid until the filtercake solids are
reversed from being oil-wet to being water-wet; and
c) electrically logging said well.

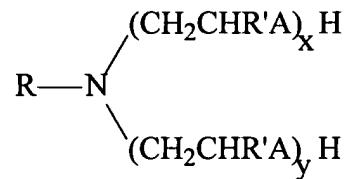
23. (NEW) The method of claim 22 wherein the invert emulsion drilling fluid is
acidified by carbon dioxide from the formation.

24. (NEW) The method of claim 22 wherein the invert emulsion drilling fluid is
acidified by hydrogen sulfide from the formation.

25. (NEW) A method of gravel packing a downhole area of a subterranean well, said
method comprising:

a) forming a mixture of a gravel packing material and an invert emulsion
drilling fluid, wherein said fluid includes: an oleaginous fluid; a non-oleaginous fluid; an
amine surfactant having the structure

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wherein R is a C₁₂-C₂₂ aliphatic hydrocarbon; R' is an independently selectable from hydrogen or C₁ to C₃ alkyl; A is NH or O, and 1 ≤ x+y ≤ 3;

- b) injecting said mixture of gravel packing material and invert emulsion into a subterranean well so as to gravel pack the downhole area ; and
- c) acidifying said fluid so as to change the oil-wet gravel packing materials into water-wet gravel packing materials and;
- d) washing said well with an aqueous based wash solution.

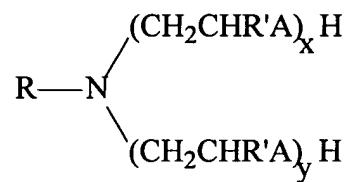
26. (NEW) The method of claim 25 wherein said fluid is acidified by carbon dioxide from the formation.

27. (NEW) The method of claim 25 wherein said fluid is acidified by hydrogen sulfide from the formation.

28. (NEW) A method of fracturing a subterranean formation, the subterranean formation being in fluid communication with the surface via a well, the method comprising:

- a) injecting a fracturing fluid into said well, wherein said fracturing fluid includes: an oleaginous fluid; and an amine surfactant having the structure

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wherein R is a C₁₂-C₂₂ aliphatic hydrocarbon; R' is an independently selectable from hydrogen or C₁ to C₃ alkyl; A is NH or O, and 1 ≤ x+y ≤ 3; and oil-wet propant material;

- b) pressurizing said fluid so as to cause the subterranean formation to fracture and allow the propant materials to enter said crack;
- c) acidifying said fluid so as to change the oil-wet propant materials into water-wet propant materials and;
- d) washing said well with an aqueous based wash solution.

29. (NEW) The method of claim 28 wherein said fluid is acidified by carbon dioxide from the formation.

30. (NEW) The method of claim 28 wherein said fluid is acidified by hydrogen sulfide from the formation.

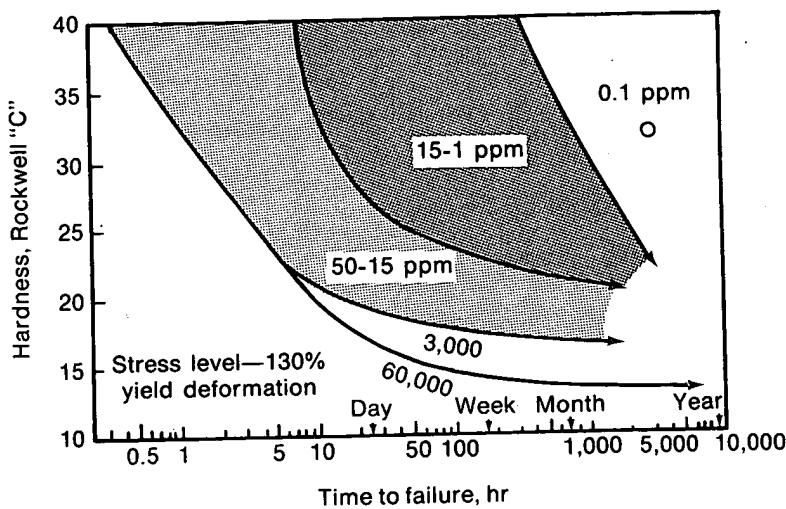


Figure 9-58. Effect of concentration of hydrogen sulfide on failure time of highly stressed steel. (From the 1970 issue of Petroleum Engineer International. Publisher retains copyright.)

Control of Corrosion

The simplest and most common method of corrosion control is to use a highly alkaline mud. There are, however, limits to this practice: Notably, degradation of clay minerals by the hydroxyl ion starts at temperatures above 200°F (93°C) when the pH of the mud is above 10. As mentioned in Chapter 5, calcium hydroxide can cause solidification of the mud at temperatures above 300°F (149°C), and all hydroxides cause significant degradation and thickening at such temperatures. The wisest policy is to maintain the pH between 9 and 10, which, in many wells, will keep corrosion within acceptable limits, and at the same time allow tannate and lignosulfonate thinners to operate most efficiently. If previous experience in the locality has shown this procedure to be inadequate for corrosion control, or if excessive corrosion is detected by examination of the steel-ring coupons (which should be included in every drill string) (see the section on corrosion tests, in Chapter 3), then treatments appropriate to the particular type of corrosion involved must be applied. Table 9-14⁷⁵ summarizes the common types of corrosion, their identification in the field, and suggested treatments. Details of the action and control of the various contaminants are as follows:

Carbon Dioxide. Carbon dioxide dissolves in water and lowers the pH by forming carbonic acid. Corrosion is best controlled by maintaining the pH between 9 and 10 with sodium hydroxide, but, when the inflow of the gas is large,

Table 9-14
Trouble Shooting Chart to Combat Drilling Fluid Corrosion*

Cause	Primary source	Visual form of attack	Corrosion by-product	Identification	
				Test	Treatment
Oxygen	Water additions	Concentration cell. Pitting under barrier or deposits	Primarily magnetic Fe_3O_4	Not acid soluble 15% HCl	Oxygen scavenger: Initial treating range equivalent of 2.5 to 10 lb/hr of sodium sulfite. Maintain 20 to 300 mg/l sulfite residual. Engineer to reduce air entrapment in pits. Defoam drilling fluid.
Air entrapment	Mixing and solids control equipment	Pits filled with black magnetic corrosion by-products		By-product attracted to magnet	Coat pipe with film forming inhibitors during trips to reduce atmospheric attack and cover concentration cell deposits.
Mineral scale deposits	Formation and mud materials	Corrosion cell pits below deposit	Iron products below mineral deposit	White mineral scale; calcium, barium and/or magnesium compounds	If mineral scale deposits on drill pipe, treat with ^t scale inhibitor at 5 to 15 mg/l or approximately 25 to 75 lb/day added slowly and continuously. Treatments of scale inhibitor may be reduced after phosphate residual exceeds 15 mg/l. Treatments of 1 gal/1000 bbl mud/day can be used for maintenance treatment under normal drilling conditions.
Aerated drilling fluid	Injected air	Severe pitting	Oxides of iron	Black to rust red	^t Organic phosphorous compounds Maintain chromate concentration at 500 to 1000 mg/l with chromate compounds or zinc chromate compounds. Maintain high pH,

(Table 9-14 continued)

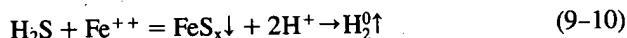
Carbon dioxide gas	Formation	Localized to pitting, dark brown to black film	Iron carbonate HCl	Slow effervescence in 15% HCl	Mineral scale precipitates can form as a result of the meta-stable reaction of carbonic acid with calcium. Scale inhibitors treatments of 5 to 15 mg/l (25 to 75 lb/day) may be required. Filming inhibitors sprayed or float-coated on drill pipe during trips.
Hydrogen sulfide gas	Formation	Localized to sharp pitting dark blue to black film on equipment †SSCC failures	Iron sulfides	Acid arsenic solution produces a bright yellow precipitate soluble in 15% HCl. Rotten egg odor. Dark blue to black film on exposed equipment. Lead acetate test.	Maintain high pH with caustic soda. Remove sulfide ions by precipitation with metal compounds, such as oxides of iron, Fe_3O_4 , and/or zinc compounds ZnCO_3 or ZnO . Sulfide 0 to 100 ppm. 3-5 lb/bbl iron oxide (Fe_3O_4) 0.1 to 0.5 lb/bbl zinc compound. The combined treatments of iron oxide and zinc compounds should provide lower sulfide ion contamination in most drilling fluids.
Atmospheric	Generalized	Iron Oxide to localized rust	Visual	Wash equipment free of salts and mud products and spray with atmospheric filming inhibitors.	

^{*} From Bush, 1974 by SPE-AIME.[†] NOTE: SSCC sulfide stress corrosion cracking produces rapid brittle failures of high strength metal (usually tool joints or bits).

the formation of excessive amounts of soluble carbonates causes high viscosities. In such cases, calcium hydroxide may be used to neutralize the acid, but the resulting calcium carbonate precipitate tends to form scale, thus setting up corrosion cells. This tendency may be offset by the use of scale inhibitors, and by cleaning the pipe during round trips.

Hydrogen Sulfide. Hydrogen sulfide may massively contaminate mud by a sudden inflow of sour gas, or gradually by the gradual degradation of lignosulfonates either by sulfate-reducing bacteria or by high temperatures. The thermal degradation of lignosulfonates starts at about 330°F (165°C) and increases gradually until a major decomposition occurs at 450°F (232°C).⁷⁶ Reaction products are hydrogen sulfide, carbon dioxide, and carbon monoxide.

Molecular hydrogen sulfide is a poisonous gas, and every possible precaution must be taken to protect rig personnel when it is encountered, even in small quantities. It is weakly acidic when dissolved in water, and attacks iron to form iron sulfides, as approximately described by the equation:



The sulfides are deposited on the pipe as a black powder.

Hydrogen sulfide ionizes in two stages, viz:



These reversible reactions are a function of pH, as shown by Figure 9-59.⁷⁸ It may be seen that the sulfide is in the form of H₂S up to about pH 6; as HS⁻ from pH 8 to 11, and as S⁻⁻ above pH 12. Since sulfide stress cracking is caused by the atomic hydrogen formed together with HS⁻ in the first ionization stage (Equation 9-11), it follows that maintaining the pH between 8 and 11 is not a viable means of control. The formation of atomic hydrogen is suppressed when the pH is above 12, but maintaining such high alkalinites is not desirable because it involves the accumulation of S⁻⁻ in the mud (Equation 9-12). Should the pH fall because of a sudden inflow of more hydrogen sulfide, or for any other reason, the ionization reactions would reverse, and large amounts of atomic hydrogen or, possibly, hydrogen sulfide gas, would be generated. A high pH is, of course, also undesirable in high temperature wells because of the aforementioned degradation of clay minerals. It is preferable, therefore, to combat hydrogen sulfide by the addition of a scavenger rather than by maintaining a high pH.

Formerly, copper salts were used to scavenge hydrogen sulfide until it was realized that these salts caused bimetallic corrosion⁷⁷ (i.e., the process shown in Figure 9-53). To prevent bimetallic corrosion, the cation of the scavenger must be higher on the electromotive series than iron. Zinc meets this qualification,

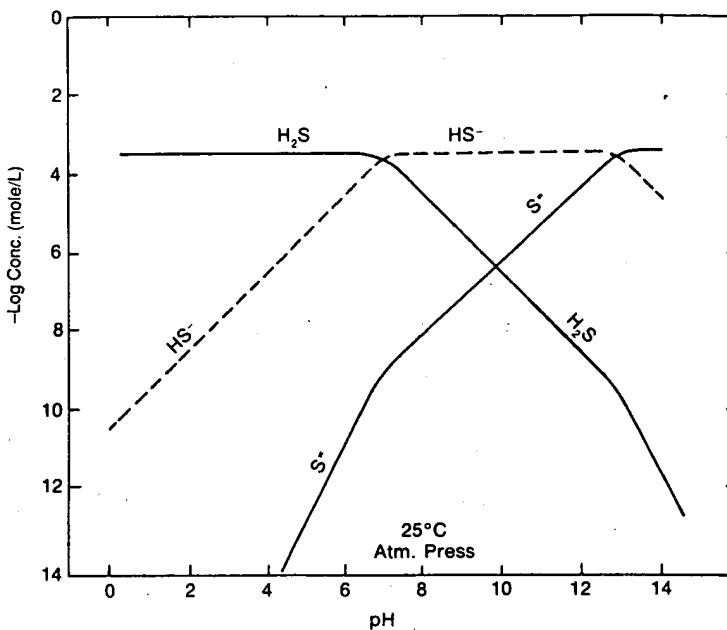


Figure 9-59. Equilibrium of the aqueous system H_2S HS^- , $\text{S}^=$, relative concentrations versus pH. (From Garrett, et al.⁷⁸ Copyright 1978 by SPE-AIME.)

and basic zinc carbonate is now commonly used. Care must be taken to maintain the pH between 9 and 11. At higher or lower pH, the solubility of zinc carbonate increases sharply and the zinc ion flocculates clay suspensions.⁷⁸ Figure 9-60 shows the consequent increase in yield point, gel strength, and filtration rate. It is evident that optimum properties are at pH 9, or thereabouts.

Flocculation by the zinc ion may be avoided by the use of a zinc chelate.⁷⁹ The zinc is held by coordinate bonds in the chelating agent so that a very low level of zinc ions is maintained in solution, but the zinc is readily available to react with the sulfide as required.

Powdered iron minerals also act as scavengers for hydrogen sulfide. For example, hydrogen sulfide reacts with iron oxides to form insoluble iron sulfides. The reaction takes place at the surface so that the efficiency of the material depends on the surface area exposed. A synthetic form of magnetite, Fe_3O_4 , which has a high specific surface because of its porous nature, is commercially available. The reaction product is pyrite, but the chemistry involved is complex, and depends on a number of variables such as pH, mud shear rate, and temperature.⁸⁰ Reaction time is fastest at low pH, and the material is therefore most effective in neutralizing sudden large influxes of hydrogen sulfide.⁸¹ The ability to operate at low pH is also an advantage in high temperature wells. Another great

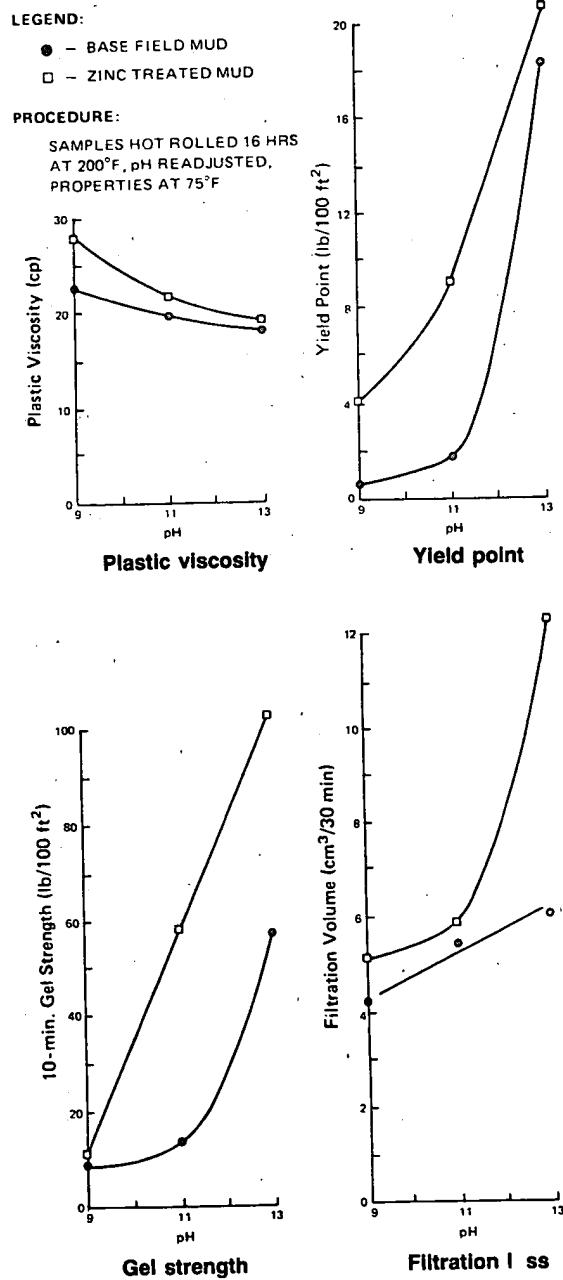


Figure 9-60. Effects of 6 lb/bbl of basic zinc carbonate on properties of an 11.8 lb/gal deflocculated field mud at 9 to 13 pH. (From Garrett, et al.⁷⁸ Copyright 1978 by SPE-AIME.)

advantage of the material is that, being insoluble, it does not affect the rheological and filtration properties of the mud.

Oxygen. Oxygen dissolved in the mud during mixing and treating operations is almost always present in drilling muds, and a few parts per million is sufficient to cause significant corrosion. Pitting, caused by the formation of oxygen corrosion cells (see Figure 9-54) under patches of rust or scale, is characteristic of oxygen corrosion.

Oxygen corrosion increases sharply with increase in temperature, and is influenced by salinity. Brines and saline muds are more corrosive than fresh water muds because of the increase in conductivity, but the corrosion rate is less at very high salinities because the solubility of oxygen is less. The effect of temperature and salinity are illustrated in Figure 9-61.⁸² Low-solid polymer muds are more corrosive than conventional high-solid muds because the tannates and lignosulfonates added to clay muds for rheological control also act as oxygen scavengers. In general, oxygen corrosion decreases with increase in pH up to about pH 12, but then increases above the value (see Figure 9-62).⁸³

The best way to prevent oxygen corrosion is to minimize the entrainment of air at the surface by using only submerged guns in the pits, and arranging for returns from desanders, desilters, etc., to discharge below the mud level. The hopper is a prime source of air entrainment, and should be used only when adding solid conditioning materials. Figure 9-63⁸⁴ shows the reduction in oxygen content when all conditioning operations were stopped.

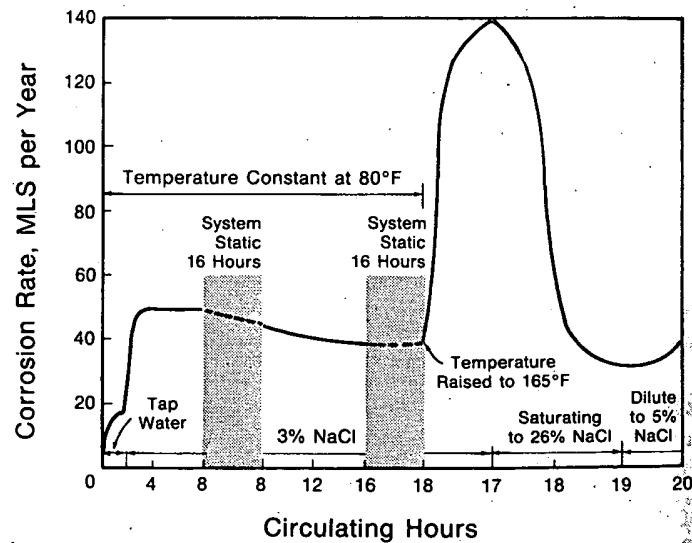


Figure 9-61. Effect of temperature and salinity on corrosion rate. (From Cox.⁸²)